CARBON MOLECULAR SIEVES DERIVED FROM POLYMERS FOR NATURAL GAS STORAGE

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ABSTRACT

In the last several years, advances have been made in the development of adsorbents for the storage of natural gas. At AlliedSignal, we have focused on the polymer-derived carbon molecular sieves for the control of micropore size, micropore volume, bulk density, and packing efficiency to enhance storage capacity. A deliverable storage efficiency of 150 volumes of methane per volume of adsorbent has been achieved at a storage pressure of 500 psig. This presentation will discuss the synthesis of the materials and the preparation and characterization of the advanced carbon molecular sieves. Structural parameters and storage capacities of these carbon molecular sieves will be compared with other carbonaceous materials. In addition, theoretical studies on determining optimum pore sizes for methane storage and molecular simulations of isotherms and isosteric heats will be presented for comparison with our carbon molecular sieves.

1. INTRODUCTION

Storage of natural gas with an adsorbent has been considered a promising technology for the on-board storage of natural gas for vehicular applications[1,2]. Among adsorbents investigated, carbon materials are most effective in the storage of natural gas at low pressures (e.g. 300-500 psig)[3]. Critical issues in the commercialization of the adsorbed natural gas storage technology include the storage capability of the adsorbent and the ease and cost of its manufacture.

The objective of the present study is to develop a high capacity carbon adsorbent which can be commercially produced at a reasonable cost. In the course of the study, molecular modeling and simulation efforts, similar to those reported by Matranga, Stella, Myers and Glandt[4], were conducted to help in the design and optimization of the pore structure of the carbon adsorbent for the storage of natural gas.

2. EXPERIMENTAL AND RESULTS

2.1 Adsorption Theory and Development of Carbon Molecular Sieves

The adsorbents developed in this study are all variants of activated carbon molecular sieves developed by AlliedSignal Inc. The development involved first understanding the theoretical basis for adsorption followed by experimentation to achieve material properties suggested from the theoretical results.

Molecular modeling and simulation were used in the optimization process for these sorbents. An understanding of the potential energy functions between methane and the carbon surface was applied to pore size control. Calculation of the second virial coefficients for adsorption, B_{1s}, as a function of graphitic carbon slit width, was performed by numerical integration of the gas-solid potential over the pore volume[5]. The maximum second virial coefficient lends insight into the optimal slit width for methane adsorption. Slits that are too large have too small a B_{1s}, due to a lack of cooperative interaction between the adsorbate and both walls of the slit. This means that the attractive forces are too small due to the large dimensional width of the pore. At too small a pore width, the repulsive forces become too large for effective adsorption. The calculation showed an optimal slit pore width of 11.4 A for methane adsorption.

Using the information from the second virial coefficient study, carbon sorbents were prepared from a proprietary polymer through a multi-step process. The carbon molecular sieve (CMS) materials were synthesized by carbonization of a proprietary polymer followed by activation with a gaseous stream to develop optimal pore structure. *Figure 2* shows a comparison of pore structures for various activated CMS materials.

The slit model and a more complex strip models which includes both structural and chemical heterogeneity were applied in order to investigate isotherms and isosteric heats of adsorption. Grand Canonical Monte Carlo (GCMC) simulations were performed. Isotherms and isosteric heats of adsorption were calculated from the fluctuations in the number of molecules and energy[6]. Figure 3 shows a heterogeneous surface of the strip model reduces the adsorption amount as compared to the homogeneous slit model. Figure 4 shows that the heterogeneous materials have isosteric heats that decrease with the coverage due to occupation of lower energy adsorption sites as coverage increases. The theoretical work shows that homogeneity of the material will enhance adsorption greatly.

2.2 Preparation and Evaluation of Carbon Molecular Sieves

The preparation of the polymer-derived carbon molecular sieves consists of four basic steps: preparation of the polymer precursor, pelletization or shaping of the precursor, carbonization, and activation of the resulting carbon molecular sieve. For the development of a high capacity adsorbent for natural gas storage, all these four process steps are investigated and optimized for volumetric storage efficiency.

2.2.1 Precursor Synthesis: A number of polymeric materials were initially screened for the ability to form microporous carbon structures with proper pore size/ pore distribution and with high carbon yield. Results of this study showed very conclusively that only a small number of polymer candidates are potentially promising. These materials include polyvinylidene chloride (PVDC), polyvinylidene fluoride, polyacrylonitrile, polychlorotrifluoroethylene, and phenolic resins. Copolyers incorporating these monomers are also potentially effective. Among these potential precursor materials, we chose to focus on the PVDC system.

Not only is the chemical nature of the monomer important but also the physical chemical properties of the polymer material. The effects of polymer molecular weight, polymer particle size and size distribution, and the density of the polymer particle were extensively studied. Synthesis method, initiation catalyst and polymerization temperature are all critical in the synthesis of the best precursor [7].

2.2.2 Pelletization and shaping of the precursor: Parameters that were found to be important for the synthesis of the adsorbent for natural gas storage are pellet configuration, pellet piece density and the uniformity of the void space throughout the pellet. During the pelletization of PVDC precursors, there were no shape additives since this may cause decreases in the volumetric/gravimetric efficiency of the resulting CMS.

2.2.3 Carbonization of the Pellet during Thermal Transformation: The PVDC precursor goes through softening, decomposition, and carbon structure formation at various temperatures. The formation of the pore structure and the density of the resulting adsorbent are critically determined by the temperature program used for the precursor pellet. Of particular importance is the fact that the PVDC precursor loses 50% of its total HCl at about 200°C and the rest of the HCl at about 500°C. The control of the kinetics of HCl evolution determines the pore size of the resulting CMS and the packing density of the adsorbent for natural gas storage.

2.2.4 Activation: The volumetric efficiency of the natural gas adsorbent is optimized by increasing the gravimetric efficiency and maintaining high packing density of the adsorbent through activation. Oxidizers such as carbon dioxide, air, and steam, and their combinations were investigated. The activation process increases the total micropore volume and modifies the pore size and pore distribution. Differences in the activation process are illustrated in Table 1.

2.2.5 Evaluation of the activated CMS: The storage efficiency of the activated carbon molecular sieves was evaluated gravimetrically. The adsorbent material was packed in a 40 mL test cell. The material was heated at 150°C under vacuum (less than 25mTorr) for a period of greater than 2 hours. Methane gas was used throughout the study to simulate the natural gas storage. The methane is introduced to the test cell at 25°C at various

pressures and the amount of methane stored was determined by weight uptake at equilibrium. The total volumetric gas storage delivery was calculated by using the total amount of methane stored per unit volume less the methane volumetric density at the delivery condition of 746 mmHg and 26.3°C, which is 0.000643 g/mL. The V/V value was determined by dividing the total deliverable gas volume with the volume of the empty test cell which was volumetrically calibrated with methane. Results of the storage measurements at 300 psig are summarized in Table 2 for comparisons with other carbon absorbents.

2.2.6 Improvement of Storage Capacity by Packing: As shown in Table 2, the volumetric efficiency of ACMS for methane storage is affected by the packing density of the absorbent material. A packing technique employing at least two sizes of absorbent particles having nominal diameters differing by at least 7:1 was developed[8]. Table 3 illustrates the improvement of deliverable V/V capacity with a binary packing system.

3. CONCLUSION

Through careful screening and parametric process optimization, a class of activated carbon molecular sieves has been developed for the on-board storage of natural gas. A deliverable volumetric capacity of 150 V/V has been achieved at 500 psig. The commercialization of this class of absorbent depends on the market need. Further studies are required to further improve the efficiency and economics of the adsorbent.

REFERENCES

1. J. Wegrzyn, H. Weismann, and T. Lee, Low Pressure Storage of Natural Gas on Activated Carbon Proceedings: Annual Automotive Tech. Develop, Dearborn, MI (1992).
2. C. R. Nelson, Physical Sciences NGV Gas Storage Research, Gas Research Institute, Chicago, IL (1993).
3. D. F. Quinn, J. A. McDonald, and K. Sosin, 207th ACS National Meeting, San Diego, CA (1994).
4. K. Matranga, A. Stella, A. Myers, and E. Glandt, Sep. Sci. and Tech. (1992) 27, 1825-1836.
5. A. Stella, "Adsorption on Activated Carbon: Comparison of Molecular Simulation with Experiment", Ph.D. Thesis, University of Pennsylvania, 1993.
6. D. Nicholson, N. G. Parsonage, "Computer Simulation and the Statistical Mechanics of Adsorption", Academic Press, London, 1982.
7. C. H. Chang, and G. J. Seminara, "Preparation of Hydrophobic Carbon Molecular Sieves", U. S. Patent #4,820,681, April 11, 1989.
8. C. H. Chang, "Packing Adsorbent Particles for Storage of Natural Gas", U. S. Patent #5,308,821, May 3, 1994.

Table 1. The Effect of Activation on the Properties of PVDC-derived CMS

Sample #	Activating gas	Activation condition (°C)	Yield after activation (%)	Packing density (g/mL)	BET surface area (m²/g)	Micropore volume (mL/g)
1	None	None	100	0.633	1484	0.45
2	Steam	825	65.8	0.435	1861	0.56
3	Steam	850	25.0	0.240	2280	1.82
4	CO2	800	73.0	0.469	1864	0.56
5	CO2	854	21.4	0.559	2145	0.65

Table 2. Storage Efficiency of Activated CMS for Methane at 25°C and 300 psig

Carbon Absorbent	Packing density (g/mL)	Storage temperature (°C)	Gravimetric efficiency (g/g)	Volumetric efficiency (V/V)
Norit carbon	0.387	24	0.1138	69
Calgon PCB	0.445	23	0.1095	76
Calgon PCB	0.500	27	0.0108	79

-Continued (Table 2)

Nuchar WV-B	0.259	25	0.1142	46
Anderson AX-21	0.355	25	0.1569	87
Saran carbon	0.320	25	0.070	51
CMS-1	0.633	25	0.1031	112
ACMS-1-1	0.545	25	0.133	122
ACMS-1-2	0.544	25	0.1401	128
ACMS-1-3	0.492	25	0.1363	115
CMS-2	1.022	25	0.1001	158
ACMS-2-1	0.837	25	0.1334	173

Table 3. Storage Efficiency of Activated CMS Systems with Binary Packing

| Adsorbent	1	2	3	4
Particles	2.3mm pellet	2.3mm pellet/beads	1.6mm pellet	1.6mm pellet/beads
Test cell (mL)	39.89	39.89	39.60	39.60
Pellet wt.(g)	21.08	21.02	21.41	21.44
Beads wt.(g)	-	5.74	-	5.43
Total dry wt (g)	20.72	26.23	21.05	26.33
Packing density (g/mL)	0.519	0.658	0.532	0.665
CH_4 adsorbed (g/g) @ 0psig	0.65	0.77	0.61	0.79
100	2.12	2.64	2.14	2.62
200	2.78	3.43	2.82	3.38
300	3.28	3.89	3.29	3.88
400	3.61	4.22	3.63	4.24
500	3.88	4.54	3.89	4.56
600	4.12	4.79	4.13	4.80
700	4.32	4.95	4.37	4.99
800	4.51	5.16	4.53	5.16
900	4.68	5.32	4.70	5.32
Deliverable V/V @ 0 psig	0	0	0	0
100	57.33	72.92	60.11	71.89
200	83.06	103.73	86.82	101.75
300	102.56	121.67	105.28	121.39
400	115.43	134.54	118.64	135.53
500	125.96	147.02	128.28	148.10
600	135.32	156.77	138.28	157.53
700	143.12	163.01	147.71	164.99
800	150.53	171.20	153.99	171.69
900	157.16	177.44	160.67	177.96
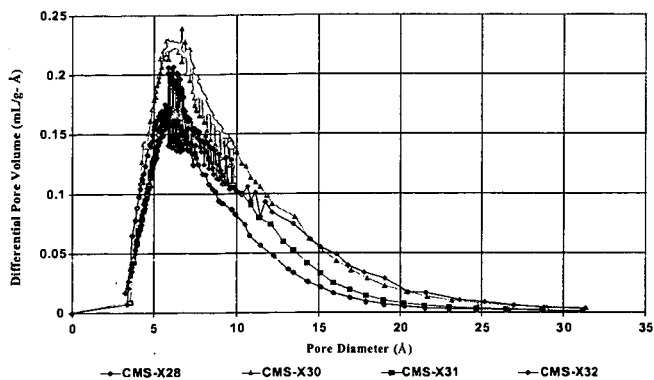
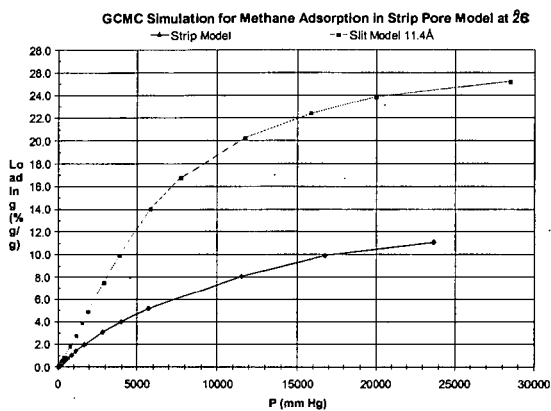**Figure 2 Horvath-Kawazoe Plot for pore structure of CMS materials**

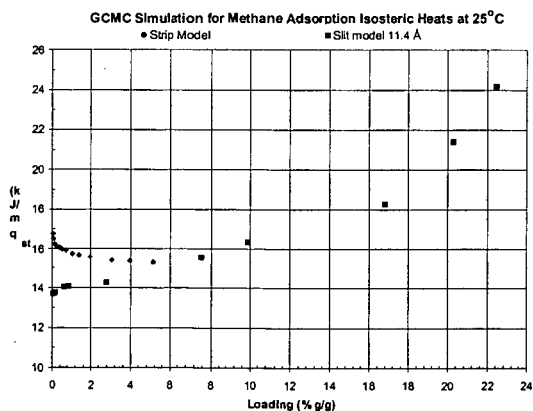*Figure 3. GCMC Simulation for Methane Adsorption in Strip Pore Model at 25°C*

Figure 4. GCMC Simulation for Methane Adsorption Isosteric Heats at 25°C